SYNTHESIS AND LIQUID-CRYSTAL PROPERTIES OF ARYL ESTERS OF p-(5-ALKYL-2-PYRIMIDINYL)BENZOIC ACIDS

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Aryl esters of p-(5-alkyl-2-pyrimidinyl)benzoic and p-(5-alkyl-2-pyrimidinyl)-benzoyloxybenzoic acids, which displayed nematic properties with broad ranges of the existence of a meso phase, particularly in the case of the diesters (up to 140-170°C), were obtained. It is shown that the presence of a 2-phenyl group in the pyrimidine ring favors the development of a liquid-crystal state as compared with 5-phenylpyrimidines.

It has been previously shown that aryl esters of 5-aryl- and 5-alkylpyrimidine-2-carboxylic acids, in contrast to the benzene analogs, do not have mesomorphism, while aryl esters of pyrimidinoyl-2-hydroxybenzoic acids display nematic properties [1, 2].

In the present research mono- (II) and diesters (III), which are isomeric with respect to the corresponding derivatives of 5-arylpyrimidines [1], were synthesized from 5-alkyl-2-pyrimidinylbenzoic acids I in order to study their liquid-crystal properties.

It is known that the planar structure of derivatives of 2-phenylpyrimidines, as compared with nonplanar 5-phenylpyrimidines [3, 4], promotes the development of packing with a layered structure [5] and thereby the development of a liquid-crystal state (for example, see [6]). On the basis of this one might have assumed that esters II and III will have better indexes with respect to liquid-crystal properties (the existence of a meso phase, its range, temperatures of phase transitions) as compared with previously studied compounds [1, 2].

Only one publication with a report regarding the liquid-crystal properties of 5-amylphenyl p-(5-propyl-2-pyrimidinyl)benzoate, which has a nematic meso phase at 77-168°C [7], is known. In contrast to the Japanese authors of the patent [7], who used derivatives of malonic ester for the construction of the pyrimidine ring, we obtained acid I by condensation of p-methoxycarbonylbenzamidine hydrochloride with aminoacroleins IV and subsequent hydrolysis of the intermediate esters V. Aryl esters II and III were obtained by the reaction of acid chlorides VI with substituted phenols or p-hydroxybenzoates in pyridine [8, 9]; however, in the case of ester IIIb it was shown that the successive two-step synthesis of diesters gives a purer product (see [10]).

Liquid-Crystal Properties of Esters II and III

As we assumed, three-ring esters II displayed liquid-crystal properties in contrast to the isomeric 5-aryl analogs [1]. A meso phase develops in 5-methyl derivative IIa, although at relatively high temperatures (Table 1). Lengthening of the alkyl radical in the 5 position of the pyrimidine ring leads to a decrease in the temperatures of the development of the nematic state. However, whereas the high-temperature transition to the isotropic meso phase is retained for cyanophenyl esters IIb, e (the range of the liquid-crystal state is expanded), a substantial decrease in the thermal stability of the meso phase is also observed for esters IIc, d.

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TABLE 1. p-(5-Alkyl-2-pyrimidinyl)benzoic Acids and Their Aryl Esters II and III

Compound	Temp. of transition,* °C		ΔT, °C†	IR spectrum, ν, cm^{-1}	Found, %			Empirical formula	Calc., %			Yield, %
	T$_{nem}$	T$_{iso}$			C	H	N (Hal)		C	H	N (Hal)	
Ia	—	277...278	—	1690	68,0	4,6	13,0	$C_{12}H_{10}N_2O_2$	67,3	4,7	13,1	84
Ib	—	219...222	—	1695	70,7	6,9	10,7	$C_{16}H_{18}N_2O_2$	71,1	6,7	10,4	92
Ic	—	216...218	—	1695	72,4	7,0	9,5	$C_{18}H_{22}N_2O_2$	72,5	7,4	9,4	80
IIa	240	289	49	1750, 2220	72,5	4,1	13,5	$C_{19}H_{13}N_3O_2$	72,4	4,1	13,3	95
IIb	120	246	126	—	74,8	5,7	11,5	$C_{23}H_{21}N_3O_2$	74,4	5,7	11,3	87
IIc	83	142	59	1730	78,2	8,2	6,2	$C_{29}H_{36}N_2O_2$	78,4	8,1	6,3	95
IId	108	146	38	1730	73,4	6,0	6,7 (4,8)	$C_{24}H_{25}FN_2O_2$	73,4	6,4	7,1 (4,8)	94
IIe	111	211	100	1740, 2250	75,1	6,8	10,7	$C_{25}H_{25}N_3O_2$	75,2	6,3	10,5	80
IIf	129	145	16	1730, 2230	67,0	5,4	9,8 (8,8)	$C_{23}H_{24}ClN_3O_2$	67,4	5,9	10,2 (8,7)	37
IIIa	114	284	170	—	76,0	8,9	5,3	$C_{34}H_{36}N_2O_4$	76,1	8,8	5,2	77
IIIb	159	325	166	1740, 2240	72,9	5,0	8,6	$C_{30}H_{28}N_3O_4$	73,2	5,1	8,5	72
IIIc	95	223	128	1740	76,6	7,3	5,1	$C_{36}H_{40}N_2O_4$	76,6	7,1	5,0	66
IIId	140	240	100	1750, 2240	73,4	6,2	8,1	$C_{32}H_{29}N_3O_4$	73,9	5,6	8,1	65
IIIe	95	237	142	1750, 2230	68,9	5,1	7,7	$C_{32}H_{28}ClN_3O_4$	69,4	5,1	7,6	65

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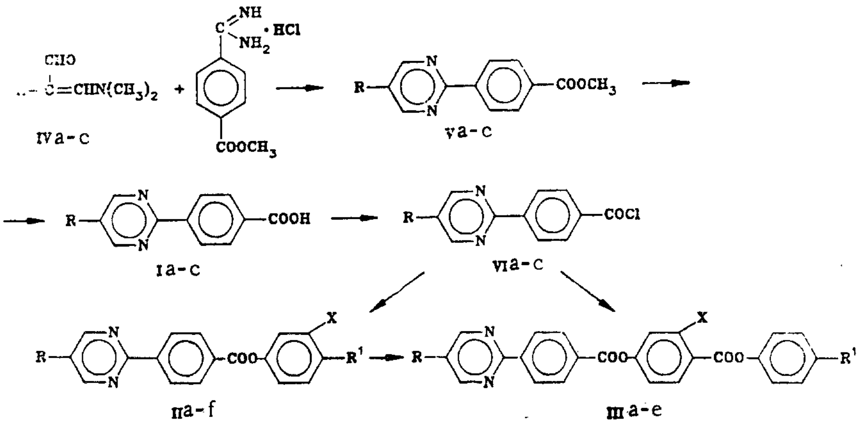
*T$_{nem}$ is the temperature of the nematic meso phase, while T$_{iso}$ is the temperature of the isotropic meso phase.

†Range of existence of the mesomorphic state.



I, II, IVa—VIa R=CH$_3$; Ib—VIb, IIIa R=C$_5$H$_{11}$; Ic—VIc, IId-f, IIId-e R=C$_7$H$_{15}$;
IIa,b,e,f IIIb,d,e R^1=CN; IIc, IIIa,c R^1=C$_5$H$_{11}$; IId R^1=F; IIa-e, IIIa-d X=H;
IIf IIIe X=Cl

A comparison with the available analogs – substituted esters of biphenylcarboxylic acid [11-13] – shows that pyrimidine esters II have, on the whole, close temperatures of the phase transitions – only a small increase in the thermal stability of the meso phase (for example, 246°C for ester IIb as compared with 231°C for the benzene analog [11]), as well as the temperature of its formation. The investigated esters II did not display a tendency to form smectics, although, for example, aromatic analog of ester IIc forms a smectic meso phase at 98-159°C [13].

The introduction of a chlorine atom into ester IIe as a side substituent gives rise to an appreciable decrease in the thermal stability of the meso phase in ester IIf. However, this decrease is smaller than that observed in the corresponding derivatives of the aromatic series [14].

Four-ring diesters III are also nematic liquid crystals over a broad temperature range (>100°C). These esters have high clarification temperatures for both the cyano and alkylphenyl derivatives; this constitutes evidence for the thermodynamic stability of the meso phase. Similar chlorine-containing four-ring diesters of the aromatic series have been described as a new class of useful liquid crystals with unusual properties [15, 16]. The pyrimidine ester IIIe that we obtained forms a nematic phase with lower temperatures of the mesomorphic transitions (by 30-60°C) than the benzene analog [15] but retains high thermal stability and a broad range of the meso phase.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The temperatures of the phase transitions were determined with a microheating stage of the Boetius with an RNMK-0.5 visual apparatus.

The characteristics of the compounds obtained are presented in Table 1.

p-(5-Alkyl-2-pyrimidinyl)benzoic Acids Ia-c. A solution of 2.25 g of sodium methoxide in 100 ml of absolute alcohol was added dropwise with stirring to a refluxing suspension of 20 mmoles of acrolein IVa-c and 20 mmoles of p-methoxycarbonylbenzamidine hydrochloride in 40 ml of absolute alcohol, after which the mixture was refluxed for 5 h and filtered. The alcohol was removed by vacuum distillation, and the residue was treated with 20 ml of 10% NaOH solution and extracted with chloroform (three 80-ml portions). The extract was washed with water (three 80-ml portions), dried with $MgSO_4$, and evaporated. A 40-ml sample of 10% NaOH solution and 10 ml of alcohol were added to the resulting ester Va-c, the mixture was refluxed for 6 h, cooled, treated with 15 ml of water, and acidified with cooling with concentrated HCl to pH 2-3. The acid was removed by filtration, washed with water, dried, and recrystallized from alcohol.

p-(5-Heptyl-2-pyrimidinyl)benzoic Acid (Ic). A mixture of 0.1 g (0.36 mmole) of 5-heptyl-2-(p-cyanophenyl)pyrimidine [17], 2 ml of 25% NaOH solution, and 3 ml of alcohol was refluxed for 6 h and then cooled, and the precipitate was removed by filtration, washed in 2 ml of water, and acidified with concentrated HCl to pH 2 to give 0.08 g (72%) of acid Ic, which was identical to the sample synthesized by the method described above.

Aryl p-(5-Alkyl-2-pyrimidinyl)benzoates IIa-f and p-[p-(5-Alkyl-2-pyrimidinyl)benzoyloxy]benzoates IIIa-e. A mixture of 2 mmoles of acid Ia-c, 5 ml of absolute benzene, and 5 ml of $SOCl_2$ was refluxed for 6 h, after which the benzene and $SOCl_2$ were removed by vacuum distillation, the residue was treated with 10 ml of benzene, and the mixture was again distilled to remove the added benzene. The resulting acid chloride VIa-c was dissolved in 7 ml of dry pyridine, 2 mmoles of the corresponding p-substituted phenol or aryl p-hydroxyphenylbenzoate was added, and the mixture was stirred for 24 h at 20°C. The reaction mixture was poured into 100 ml of a 12% solution of HCl containing ice. The precipitate was removed by filtration, washed with water (two 25-ml portions), dried, and recrystallized from ethyl acetate (IIb, IIIa, c), from hexane (IIc, d), from ethyl acetate—acetonitrile (IIa, e), from ethyl acetate—pentane (IIf, IIId), from alcohol and ethyl acetate (IIIb), and from petroleum ether (IIIe).

5-Cyanophenyl p-[p-(5-Amyl-2-pyrimidinyl)benzoyloxy]benzoate (IIIb). A mixture of 0.5 g (1.9 mmoles) of acid Ib, 5 mm of $SOCl_2$, and 5 ml of absolute benzene was refluxed for 7 h, after which the benzene and $SOCl_2$ were removed by vacuum distillation, the residue was treated with 10 ml of absolute benzene, and the mixture was again distilled to dryness to remove the added benzene. The acid chloride VIb thus obtained was dissolved in 5 ml of dry pyridine and treated with 0.27 g (1.9 mmoles) of p-hydroxybenzoic acid, and the mixture was stirred for 24 h at 20°C. The reaction mixture was poured into 50 ml of 3 N HCl containing ice, and the precipitate was removed by filtration, washed with water (three 20-ml portions), and dried to give 0.63 g (83%) of p-carboxyphenyl p-(5-amyl-2-pyrimidinyl)benzoate (IR spectrum: 1695, 1730 cm^{-1}). The resulting ester was treated with 6 ml of $SOCl_2$ and 5 ml of absolute benzene, and the mixture was refluxed for 11 h. After the previously described standard workup of the reaction mixture, p-[p-(5-amyl-2-pyrimidinyl)benzoyloxy]benzoate was obtained. The latter was dissolved to 10 ml of dry pyridine, 0.21 g of p-hydroxybenzonitrile was added, and the mixture was stirred for 24 h at 20°C. It was then poured into 150 ml of 3 N HCl containing ice. The resulting ester IIIb [0.63 g (73%)] was recrystallized from ethyl acetate.

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NMR SPECTRA OF CYCLIC NITRONES.

4.* SYNTHESIS AND ^{13}C NMR SPECTRA OF 4H-IMIDAZOLE N-OXIDES AND N,N-DIOXIDES

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4H-Imidazole 1,3-dioxides and 4H-imidazole 3-oxides were obtained by oxidation of 1-hydroxy-3-imidazoline 3-oxides and 1-hydroxy-3-imidazolines with lead and manganese dioxides or the stable nitroxyl radical, while 4H-imidazole 1-oxides were obtained by thermal decomposition of 1-acetoxy-3-imidazoline 3-oxides. Facile oxidation of the ethyl group in 5-ethyl-4H-imidazole 1,3-dioxide and the formation of 5-acetyl-4H-imidazole 1,3-dioxide and 5-acetyl-4H-imidazole 3-oxide were observed. It is shown that a strictly determined region of chemical shifts of the $C_{(2)}$, $C_{(5)}$, and $C_{(4)}$ atoms is characteristic for each group of 4H-imidazole N-oxides in the ^{13}C NMR spectra; this makes it possible to clearly establish the position of the N-oxide oxygen atom.

Continuing our study of the NMR spectra of cyclic nitrones [1-3] we have examined the spectral characteristics of conjugated heterocyclic nitrones – 4H-imidazole N-oxides and N,N-dioxides. The interest in these few compounds, which have received little study [4], is due to the peculiarity of their chemical properties such as their ability to undergo facile covalent hydration [5] and the recently observed property of being able to undergo conversion to heterocyclic nitroxyl radicals, the structure of which depends on the orientation of the N-oxide groups in the 4H-imidazole. The methods that we used to obtain 4H-imidazole N-oxides and N,N-dioxides lead to compounds with known positions and numbers of N-oxide groups. Using these compounds as a base we compared the possibilities of various spectral methods for the determination of the structures of these compounds, viz., the

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*See [1] for Communication 3.

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